DISPERSED FLUORESCENCE SPECTRA AND GROUND STATE POTENTIAL OF R·SH COMPLEXES (R = Ne, Ar AND Kr)

MIN-CHIEH YANG AND TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

The dispersed fluorescence spectra of R·SH have been observed following laser excitation of specific excited $\tilde{A}^2\Sigma^+$ vibronic levels. There are three possible emission mechanisms: (1)re-emission from the pumped level, (2) relaxation to lower vibrational levels and emission therefrom, and (3) a dissociation mechanism : R·SH $\rightarrow$ R + SH* $\rightarrow$ R + SH + hν. This latter mechanism has little contribution because the lifetime of the excited state SH is very short ($<$ 3 ns); therefore most of the SH will dissociate rather then emitting photons. Mechanisms (1) and (2) can be separated by careful comparison of spectra from adjacent vibrational levels. From the resulting analysis much can be learned about the $\tilde{X}^2\Pi$ state's vibrational structure. The ground states of R·SH can be described as near the free rotor limit. Most of the observed emission features are terminated on the internal SH-rotor levels in the ground state but in Ne·SH and Ar·SH, transitions to levels associated with excitation of the R-SH stretch are also observed. Due to the experimental resolution (10cm^{-1}) one does not resolve the P structure in the ground state. Using the dispersed fluorescence data, the ground state angular potential can be fit to the model developed by Dubernet et al.[a] The details of the analysis will be presented.

[a]M.-L. Dubernet, D. Flower, and J. M. Hutson, *J. Phys. Chem.* **94**, 7602 (1991)